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PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of	Docket No: Q66049
KONUMA, Hiroshi, et al.	Allowed: June 16, 2004
Appln. No.: 09/963,331	Group Art Unit: 1751
Confirmation No.: 9823	Examiner: Derrick G. Hamlin
Filed: September 26, 2001	

For: SOLID ELECTROLYTIC CAPACITOR AND METHOD FOR PRODUCING THE SAME

REQUEST FOR ACKNOWLEDGMENT OF APPLICANTS' CLAIM TO DOMESTIC PRIORITY AND RECEIPT OF VERIFIED ENGLISH TRANSLATIONS OF PROVISIONAL APPLICATIONS

MAIL STOP ISSUE FEE
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

Applicants respectfully request the Examiner to acknowledge Applicants' claim for domestic priority under 35 U.S.C. § 119 (e) based on Provisional Application Nos. 60/106,967, 60/106,968 and 60/106,969 filed on November 4, 1998. In addition, Applicants submit herewith copies of the verified English translations. The Examiner is respectfully requested to acknowledge receipt of the verified English translations thereof filed in the provisional applications.

Applicants respectfully request the Examiner to acknowledge Applicants' claim to domestic priority and acknowledge receipt of the verified English translations of Provisional Application Nos. 60/106,967, 60/106,968 and 60/106,969.

Respectfully submitted,

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Date: September 8, 2004

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DECLARATION

I, Atsuko Ikeda, residing at 26-2-906, Ojima 3-chome, Koto-ku, Tokyo, Japan, do hereby certify that I am conversant with the English and Japanese languages and am a competent translator thereof. I further certify that to the best of my knowledge and belief the attached English translation is a true and correct translation made by me of U.S. Provisional Patent Application No. 60/106,967 filed on November 4, 1998.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this 27th day of January, 1999

Atsuko Ikeda

Atsuko Ikeda

[NAME OF DOCUMENT] Specification

[TITLE OF THE INVENTION]

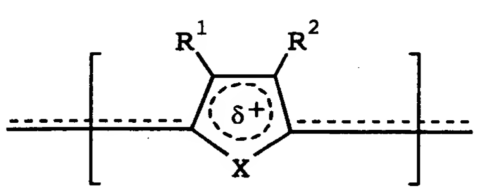
Solid Electrolytic Capacitor and Method for Producing the Same

[SCOPE OF CLAIM FOR PATENT]

[Claim 1] A solid electrolytic capacitor comprising an oxide dielectric film having provided thereon an electrically conducting polymer composition layer, wherein said composition contains from 0.1 to 50 wt% of a sulfoquinone anion having one or more sulfoanion groups and a quinone structure within the molecule and from 0.1 to 10 wt% of an anion other than said sulfoquinone anion.

[Claim 2] A solid electrolytic capacitor comprising an oxide dielectric film having provided thereon an electrically conducting polymer composition layer, wherein the electrically conducting polymer in said composition has a main chain containing a structural unit represented by the following formula (I):

[Chem. 1]



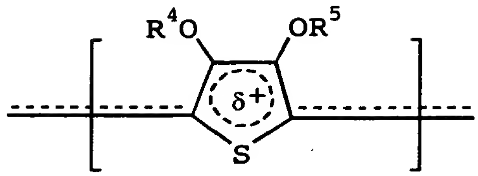
(I)

(wherein the substituents R^1 and R^2 each independently represents hydrogen, a linear or branched, saturated or

unsaturated alkyl group having from 1 to 6 carbon atoms or any one monovalent group selected from a linear or branched, saturated or unsaturated alkoxy group having from 1 to 6 carbon atoms, a hydroxyl group, a halogen atom, a nitro group, a cyano group, a trihalomethyl group, a phenyl group and a substituted phenyl group, R^1 and R^2 may be combined to each other at any position to form at least one divalent chain for forming at least one 5-, 6- or 7-membered saturated or unsaturated ring structure, X represents a hetero atom selected from S, O, Se, Te or NR^3, R^3 represents H, a linear or branched, saturated or unsaturated alkyl group having from 1 to 6 carbon atoms, a phenyl group or a linear or branched, saturated or unsaturated alkoxy group having from 1 to 6 carbon atoms, the alkyl group and the alkoxy group represented by R^1, R^2 or R^3 may optionally contain in the chain thereof a carbonyl bond, an ether bond, an ester bond, an amide bond or an imino bond, and δ represents a number of from 0 to 1).

[Claim 3] The solid electrolytic capacitor as claimed in claim 2, wherein the structural unit represented by formula (I) is a chemical structure represented by the following formula (II):

[Chem. 2]



(II)

(wherein the substituents R^4 and R^5 each independently represents hydrogen, a linear or branched, saturated or unsaturated alkyl group having from 1 to 6 carbon atoms or a substituent for forming at least one 5-, 6- or 7-membered heterocyclic structure containing the two oxygen elements shown in the formula by combining the alkyl groups each having from 1 to 6 carbon atoms to each other at any position, the ring structure formed in the scope thereof includes a chemical structure such as a substituted vinylene group and a substituted o-phenylene group, and δ represents a number of from 0 to 1).

[Claim 4] The solid electrolytic capacitor as claimed in claims 1 to 3, wherein the basic skeleton of the sulfoquinone anion is at least one anion selected from the group consisting of p-benzoquinone, o-benzoquinone, 1,2-naphthoquinone, 1,4-naphthoquinone, 2,6-naphthoquinone, 9,10-anthraquinone (hereinafter simply referred to as an "anthraquinone"), 1,4-anthraquinone, 1,2-anthraquinone, 1,4-chrysenequinone, 5,6-chrysenequinone, 6,12-chrysenequinone, acenaphthoquinone, acenaphthenequinone,

camphorquinone, 2,3-bornanedione, 9,10-phenanthrenequinone and 2,7-pyrenequinone.

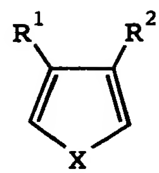
[Claim 5] The solid electrolytic capacitor as claimed in claim 4, wherein the sulfoquinone contains a sulfoquinone having one or more sulfoanion groups and a quinone structure within the molecule, a hydroquinone structure moiety produced from said quinone and/or said quinhydrone structure moiety.

[Claim 6] The solid electrolytic capacitor as claimed in claims 1 to 5, wherein the anion other than a sulfoquinone anion is a reductant anion of an oxidizing agent.

[Claim 7] The solid electrolytic capacitor as claimed in claim 6, wherein the reductant anion of an oxidizing agent is a sulfate ion.

[Claim 8] A method for producing a solid electrolytic capacitor comprising an oxide dielectric film having provided thereon an electrically conducting polymer composition described in claims 1 to 7, said method comprising polymerizing a monomer compound on an oxide dielectric film by an oxidizing agent, wherein the monomer compound is a compound represented by the following formula (III):

[Chem. 3]

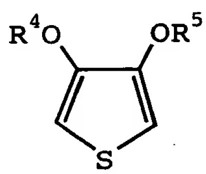


(III)

(wherein R^1, R^2 and X are the same as defined in formula (I)) and said polymerization reaction is effected in the presence of a compound capable of providing a sulfoquinone anion.

[Claim 9] The method for producing a solid electrolytic capacitor as claimed in claim 8, wherein the monomer compound represented by formula (III) is a compound represented by the following formula (IV):

[Chem. 4]



(IV)

(wherein R^4 and R^5 are the same as defined in formula (II)).

[Claim 10] A method for producing a solid electrolytic capacitor comprising an oxide dielectric film having provided thereon an electrically conducting polymer composition described in claims 1 to 9, said method comprising polymerizing a monomer compound on an oxide dielectric film by an oxidizing agent, which comprises a step of dipping a valve acting metal anode foil having

formed thereon an oxide dielectric film layer in a solution containing the monomer compound and a step of dipping the metal anode foil in a solution containing the oxidizing agent and a sulfoquinone anion.

[Claim 11] A method for producing a solid electrolytic capacitor comprising an oxide dielectric film having provided thereon an electrically conducting polymer composition described in claims 1 to 9, said method comprising polymerizing a monomer compound on an oxide dielectric film by an oxidizing agent, which comprises a step of dipping a valve acting metal anode foil having formed thereon an oxide dielectric film layer in a solution containing the oxidizing agent and a step of dipping the metal anode foil in a solution containing the monomer compound and a sulfoquinone anion.

[Claim 12] A method for producing a solid electrolytic capacitor comprising an oxide dielectric film having provided thereon an electrically conducting polymer composition described in claims 1 to 9, said method comprising polymerizing a monomer compound on an oxide dielectric film by an oxidizing agent, which comprises a step of dipping a valve acting metal anode foil having formed thereon an oxide dielectric film layer in a solution containing the oxidizing agent and then dipping the metal anode foil in a solution containing the monomer compound

and a sulfoquinone anion.

[Claim 13] A method for producing a solid electrolytic capacitor comprising an oxide dielectric film having provided thereon an electrically conducting polymer composition described in claims 1 to 9, said method comprising polymerizing a monomer compound on an oxide dielectric film by an oxidizing agent, which comprises a step of dipping a valve acting metal anode foil having formed thereon an oxide dielectric film layer in a solution containing the monomer compound and then dipping the metal anode foil in a solution containing the oxidizing agent and a sulfoquinone anion.

[Claim 14] A method for producing a solid electrolytic capacitor comprising an oxide dielectric film having provided thereon an electrically conducting polymer composition described in claims 1 to 9, said method comprising polymerizing a monomer compound on an oxide dielectric film by an oxidizing agent, which comprises a step of dipping a valve acting metal anode foil having formed thereon an oxide dielectric film layer in a solution containing the oxidizing agent and a sulfoquinone anion and then dipping the metal anode foil in a solution containing the monomer compound.

[Claim 15] A method for producing a solid electrolytic capacitor comprising an oxide dielectric film

having provided thereon an electrically conducting polymer composition described in claims 1 to 9, said method comprising polymerizing a monomer compound on an oxide dielectric film by an oxidizing agent, which comprises a step of dipping a valve acting metal anode foil having formed thereon an oxide dielectric film layer in a solution containing the monomer compound and a sulfoquinone anion and then dipping the metal anode foil in a solution containing the oxidizing agent.

[Claim 16] A method for producing a solid electrolytic capacitor comprising an oxide dielectric film having provided thereon an electrically conducting polymer composition described in claims 1 to 9, said method comprising polymerizing a monomer compound on an oxide dielectric film by an oxidizing agent, which comprises a step of repeating multiple times a process of dipping a valve acting metal anode foil having formed thereon an oxide dielectric film layer in a solution containing the oxidizing agent and a sulfoquinone anion and then dipping the metal anode foil in a solution containing the monomer compound.

[Claim 17] A method for producing a solid electrolytic capacitor comprising an oxide dielectric film having provided thereon an electrically conducting polymer composition described in claims 1 to 9, said method

comprising polymerizing a monomer compound on an oxide dielectric film by an oxidizing agent, which comprises a step of repeating multiple times a process of dipping a valve acting metal anode foil having formed thereon an oxide dielectric film layer in a solution containing the monomer compound and a sulfoquinone anion and then dipping the metal anode foil in a solution containing the oxidizing agent.

[Claim 18] A method for producing a solid electrolytic capacitor comprising an oxide dielectric film having provided thereon an electrically conducting polymer composition described in claims 1 to 9, said method comprising polymerizing a monomer compound on an oxide dielectric film by an oxidizing agent, which comprises a step of repeating multiple times a process of dipping a valve acting metal anode foil having formed thereon an oxide dielectric film layer in a solution containing the oxidizing agent and then dipping the metal anode foil in a solution containing the monomer compound and a sulfoquinone anion.

[Claim 19] A method for producing a solid electrolytic capacitor comprising an oxide dielectric film having provided thereon an electrically conducting polymer composition described in claims 1 to 9, said method comprising polymerizing a monomer compound on an oxide

dielectric film by an oxidizing agent, which comprises a step of repeating multiple times a process of dipping a valve acting metal anode foil having formed thereon an oxide dielectric film layer in a solution containing the monomer compound and then dipping the metal anode foil in a solution containing the oxidizing agent and a sulfoquinone anion.

[Claim 20] A method for producing a solid electrolytic capacitor comprising an oxide dielectric film having provided thereon an electrically conducting polymer composition described in claims 1 to 9, said method comprising polymerizing a monomer compound on an oxide dielectric film by an oxidizing agent, wherein a process of dipping a valve acting metal anode foil having formed thereon an oxide dielectric film layer in a solution containing the oxidizing agent and a sulfoquinone anion and then dipping the metal anode foil in a solution containing the monomer compound is repeated multiple times and thereafter the metal anode foil is washed and dried.

[Claim 21] A method for producing a solid electrolytic capacitor comprising an oxide dielectric film having provided thereon an electrically conducting polymer composition described in claims 1 to 9, said method comprising polymerizing a monomer compound on an oxide dielectric film by an oxidizing agent, wherein a process of

dipping a valve acting metal anode foil having formed thereon an oxide dielectric film layer in a solution containing the monomer compound and a sulfoquinone anion and then dipping the metal anode foil in a solution containing the oxidizing agent is repeated multiple times and thereafter the metal anode foil is washed and dried.

[Claim 22] A method for producing a solid electrolytic capacitor comprising an oxide dielectric film having provided thereon an electrically conducting polymer composition described in claims 1 to 9, said method comprising polymerizing a monomer compound on an oxide dielectric film by an oxidizing agent, wherein a process of dipping a valve acting metal anode foil having formed thereon an oxide dielectric film layer in a solution containing the oxidizing agent and then dipping the metal anode foil in a solution containing the monomer compound and a sulfoquinone anion is repeated multiple times and thereafter the metal anode foil is washed and dried.

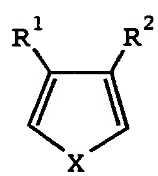
[Claim 23] A method for producing a solid electrolytic capacitor comprising an oxide dielectric film having provided thereon an electrically conducting polymer composition described in claims 1 to 9, said method comprising polymerizing a monomer compound on an oxide dielectric film by an oxidizing agent, wherein a process of dipping a valve acting metal anode foil having formed thereon

thereon an oxide dielectric film layer in a solution containing the monomer compound and then dipping the metal anode foil in a solution containing the oxidizing agent and a sulfoquinone anion is repeated multiple times and thereafter the metal anode foil is washed and dried.

[Claim 24] The method for producing a solid electrolytic capacitor as claimed in claim 8 or 9, wherein the oxidizing agent is a persulfate.

[Claim 25] The method for producing a solid electrolytic capacitor as claimed in claim 10 to 23, wherein the oxidizing agent is a persulfate and the monomer compound is a compound represented by the following formula (III):

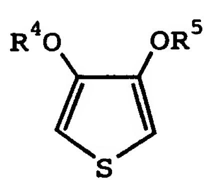
[Chem. 5]



(III)

(wherein R^1, R^2 and X are the same as defined in formula (I)) or a compound represented by the following formula (IV):

[Chem. 6]



(IV)

(wherein R^4 and R^5 are the same as defined in formula (II)).

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Technical Field to Which the Invention Belongs]

The present invention relates to a solid electrolytic capacitor and a production method thereof. More specifically, the present invention relates to a solid electrolytic capacitor comprising a solid electrolyte formed of an electrically conducting polymer composition containing a sulfoquinone having one or more sulfoanion groups and a quinone structure within the molecule and as a dopant, another anion having a dopant ability, and a production method of the capacitor.

[0002]

[Background Art]

A solid electrolytic capacitor is a device where an oxide film layer is formed on an anode substrate comprising a metal foil subjected to etching treatment, a solid semiconductor layer (hereinafter simply referred to as a solid electrolyte) is formed as an opposing electrode outside the dielectric layer and preferably an electric conductor layer such as an electrically conducting paste is further formed. The device is actually used after the entire device is completely sealed by an epoxy resin or the like.

[0003]

For the solid electrolyte, it has been heretofore known to use, for example, an inorganic semiconductor material such as manganese dioxide and lead dioxide, a TCNQ complex salt, an intrinsic electrically conducting polymer having an electric conductivity of from 10^{-3} to 5×10^{3} S/cm (JP-A-1-169914 (the term "JP-A" as used herein means an "unexamined published Japanese patent application")) or a π-conjugated polymer such as polyaniline (JP-A-61-239617), polypyrrole (JP-A-61-240625), polythiophene derivative (JP-A-2-15611) or polyisothianaphthene (JP-A-62-118511). Many of these electrically conducting polymers comprising a π-conjugated structure are used as a composition containing a dopant. Furthermore, in recent years, not only a dopant is added but also a compound containing, for example, manganese dioxide (JP-B-6-101418 (the term "JP-B" as used herein means an "examined Japanese patent publication") or a filler (JP-A-9-320901) is used in combination.

[0004]

With respect to the method for forming a solid electrolyte, a method of forming by fusion a solid electrolyte on a dielectric layer provided on a valve-acting metal surface having a fine void structure as described above or a method of producing the above-described electrically conducting polymer on a dielectric

layer has been conventionally used. To speak more specifically, for example, in the case of using a polymer of a 5-membered heterocyclic compound such as pyrrole or thiophene is used, a method where an anode foil is dipped in a lower alcohol/water-based solution of a 5-membered heterocyclic compound and then dipped in an aqueous solution having dissolved therein an oxidizing agent and an electrolyte to give rise to chemical polymerization, thereby forming an electrically conducting polymer (JP-A-5-175082), and a method where a 3,4-dioxyethylenethiophene monomer and an oxidizing agent each preferably in the form of a solution are applied separately differing in time or simultaneously onto an oxide coating layer of a metal foil to thereby form a solid electrolyte layer (JP-A-2-15611 and JP-A-10-32145) are known. In particular, JP-A-10-32145 describes a capacitor using a poly(3,4-dioxyethylene-thiophene) having doped with a specific organic sulfonic acid such as benzoquinonesulfonic acid or alicyclic sulfonic acid, stating that excellent effects are attained on the high temperature resistance or prevention of deterioration in the capacitance.

Known examples of the oxidizing agent which can give rise to chemical polymerization of a 5-membered heterocyclic compound such as thiophene include iron(III) chloride, $Fe(ClO_4)_3$, organic acid iron(III), inorganic acid

iron(III), alkylpersulfate, ammonium persulfate (hereinafter simply referred to as "APS"), hydrogen peroxide and $K_2Cr_2O_7$ (see, JP-A-2-15611).

[0005]

[Problems to be Solved by the Invention]

However, the capacitor comprising a solid electrolyte of manganese dioxide is disadvantageous in that the oxide film layer is ruptured at the thermal decomposition of manganese nitrate and the impedance property is not satisfactory. Use of lead dioxide is not preferred in view of adverse effect on the environment. The capacitor using a TCNQ complex salt solid electrolyte has good heat fusion workability and excellent electric conductivity but the TCNQ complex salt itself has a problem in the heat resistance and accordingly, the soldering heat resistance is poorly reliable. In order to overcome these problems, an electrically conducting polymer such as polypyrrole is applied to the solid electrolyte on the surface of a dielectric by electrolytic polymerization or chemical polymerization but satisfactory results cannot be obtained with respect to the homogeneity of film, soldering heat resistance, impedance property and the like.

[0006]

Demands for production of a capacitor device having high performance are recently increasing and to cope with

this, further improvements are required on the material for the solid electrolyte, production method thereof, heat stability, homogeneity of the film and the like. Under these circumstances, the object of the present invention is to provide a solid electrolytic capacitor having excellent properties satisfying the requirements with respect to the reduction in the weight, high capacity, high frequency property, tan δ, leakage current, heat resistance (reflow property), durability, etc. In particular, the object of the present invention is to provide a heat resistant solid electrolytic capacitor having excellent low impedance property and exhibiting durability in a sparking voltage test.

[0007]

[Means to Solve the Problems]

In order to attain the above-described objects, the kind, combination and content of a dopant anion in the electrically conducting polymer composition which works out to a solid electrolyte have been extensive investigated. As a result, the present invention provides a solid electrolytic capacitor comprising opposing electrodes, one part electrode being a dielectric layer comprising a metal oxide and having a fine structure provided on the surface of a valve-acting metal foil, and a solid electrolyte comprising an electrically conducting polymer composition

formed on the dielectric layer, wherein the solid electrolyte contains a sulfoquinone having one or more sulfoanion groups and a quinone structure within the molecular and further contains another anion having a dopant ability as a dopant other than the above-described quinone. This is a compact and high-performance solid electrolytic capacitor having low impedance and exhibiting durability in a sparking voltage test. The present invention also provides a production method of the solid electrolytic capacitor.

[0008]

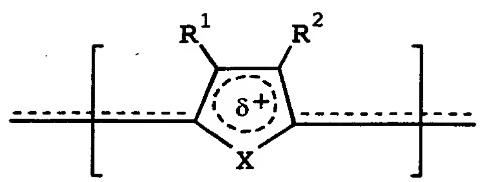
More specifically, the present invention provides the following solid catalytic capacitors and production methods thereof.

[1] A solid electrolytic capacitor comprising an oxide dielectric film having provided thereon an electrically conducting polymer composition layer, wherein the composition contains from 0.1 to 50 wt% of a sulfoquinone anion having one or more sulfoanion groups and a quinone structure within the molecule and from 0.1 to 10 wt% of an anion other than said sulfoquinone anion.

[2] A solid electrolytic capacitor comprising an oxide dielectric film having provided thereon an electrically conducting polymer composition layer, wherein the electrically conducting polymer in the composition has

a main chain containing a structural unit represented by the following formula (I):

[Chem. 7]



(I)

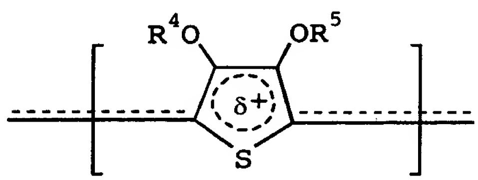
(wherein the substituents R^1 and R^2 each independently represents hydrogen, a linear or branched, saturated or unsaturated alkyl group having from 1 to 6 carbon atoms or any one monovalent group selected from a linear or branched, saturated or unsaturated alkoxy group having from 1 to 6 carbon atoms, a hydroxyl group, a halogen atom, a nitro group, a cyano group, a trihalomethyl group, a phenyl group and a substituted phenyl group, R^1 and R^2 may be combined to each other at any position to form at least one divalent chain for forming at least one 5-, 6- or 7-membered saturated or unsaturated ring structure, X represents a hetero atom selected from S, O, Se, Te or NR^3, R^3 represents H, a linear or branched, saturated or unsaturated alkyl group having from 1 to 6 carbon atoms, a phenyl group or a linear or branched, saturated or unsaturated alkoxy group having from 1 to 6 carbon atoms, the alkyl group and the alkoxy group represented by R^1, R^2 or R^3 may optionally contain in the chain thereof a carbonyl bond, an ether bond,

an ester bond, an amide bond or an imino bond, and δ represents a number of from 0 to 1).

[0009]

[3] The solid electrolytic capacitor as described in [2], wherein the structural unit represented by formula (I) is a chemical structure represented by the following formula (II):

[Chem. 8]



(II)

(wherein the substituents R^4 and R^5 each independently represents hydrogen, a linear or branched, saturated or unsaturated alkyl group having from 1 to 6 carbon atoms or a substituent for forming at least one 5-, 6- or 7-membered heterocyclic structure containing the two oxygen elements shown in the formula by combining the alkyl groups each having from 1 to 6 carbon atoms to each other at any position, the ring structure formed in the scope thereof includes a chemical structure such as a substituted vinylene group and a substituted o-phenylene group, and δ represents a number of from 0 to 1).

[4] The solid electrolytic capacitor as described in [1] to [3], wherein the basic skeleton of the sulfoquinone

anion is at least one anion selected from the group consisting of p-benzoquinone, o-benzoquinone, 1,2-naphthoquinone, 1,4-naphthoquinone, 2,6-naphthoquinone, 9,10-anthraquinone (hereinafter simply referred to as an "anthraquinone"), 1,4-anthraquinone, 1,2-anthraquinone, 1,4-chrysenequinone, 5,6-chrysenequinone, 6,12-chrysenequinone, acenaphthoquinone, acenaphthenequinone, camphorquinone, 2,3-bornanedione, 9,10-phenanthrenequinone and 2,7-pyrenequinone.

[0010]

[5] The solid electrolytic capacitor as described in [4], wherein the sulfoquionone contains a sulfoquinone having one or more sulfoanion groups and a quinone structure within the molecule, a hydroquinone structure moiety produced from the quinone and/or the quinhydrone structure moiety.

[6] The solid electrolytic capacitor as described in [1] to [5], wherein the anion other than a sulfoquinone anion is a reductant anion of an oxidizing agent.

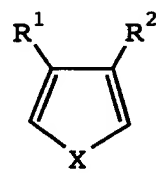
[7] The solid electrolytic capacitor as described in [6], wherein the reductant anion of an oxidizing agent is a sulfate ion.

[0011]

[8] A method for producing a solid electrolytic capacitor comprising an oxide dielectric film having

provided thereon an electrically conducting polymer composition described in [1] to [7], the method comprising polymerizing a monomer compound on an oxide dielectric film by an oxidizing agent, wherein the monomer compound is a compound represented by the following formula (III):

[Chem. 9]

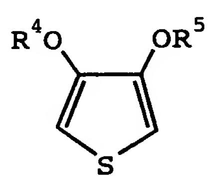


(III)

(wherein R^1, R^2 and X are the same as defined in formula (I)) and said polymerization reaction is effected in the presence of a compound capable of providing a sulfoquinone anion.

[9] The method for producing a solid electrolytic capacitor as described in [8], wherein the monomer compound represented by formula (III) is a compound represented by the following formula (IV):

[Chem. 10]



(IV)

(wherein R^4 and R^5 are the same as defined in formula (II)).

[0012]

[10] A method for producing a solid electrolytic

capacitor comprising an oxide dielectric film having provided thereon an electrically conducting polymer composition described in [1] to [9], the method comprising polymerizing a monomer compound on an oxide dielectric film by an oxidizing agent, which comprises a step of dipping a valve acting metal anode foil having formed thereon an oxide dielectric film layer in a solution containing the monomer compound and a step of dipping the metal anode foil in a solution containing the oxidizing agent and a sulfoquinone anion.

[11] A method for producing a solid electrolytic capacitor comprising an oxide dielectric film having provided thereon an electrically conducting polymer composition described in [1] to [9], the method comprising polymerizing a monomer compound on an oxide dielectric film by an oxidizing agent, which comprises a step of dipping a valve acting metal anode foil having formed thereon an oxide dielectric film layer in a solution containing the oxidizing agent and a step of dipping the metal anode foil in a solution containing the monomer compound and a sulfoquinone anion.

[12] A method for producing a solid electrolytic capacitor comprising an oxide dielectric film having provided thereon an electrically conducting polymer composition described in [1] to [9], the method comprising

polymerizing a monomer compound on an oxide dielectric film by an oxidizing agent, which comprises a step of dipping a valve acting metal anode foil having formed thereon an oxide dielectric film layer in a solution containing the oxidizing agent and then dipping the metal anode foil in a solution containing the monomer compound and a sulfoquinone anion.

[0013]

[13] A method for producing a solid electrolytic capacitor comprising an oxide dielectric film having provided thereon an electrically conducting polymer composition described in [1] to [9], the method comprising polymerizing a monomer compound on an oxide dielectric film by an oxidizing agent, which comprises a step of dipping a valve acting metal anode foil having formed thereon an oxide dielectric film layer in a solution containing the monomer compound and then dipping the metal anode foil in a solution containing the oxidizing agent and a sulfoquinone anion.

[14] A method for producing a solid electrolytic capacitor comprising an oxide dielectric film having provided thereon an electrically conducting polymer composition described in [1] to [9], the method comprising polymerizing a monomer compound on an oxide dielectric film by an oxidizing agent, which comprises a step of dipping a

valve acting metal anode foil having formed thereon an oxide dielectric film layer in a solution containing the oxidizing agent and a sulfoquinone anion and then dipping the metal anode foil in a solution containing the monomer compound.

[15] A method for producing a solid electrolytic capacitor comprising an oxide dielectric film having provided thereon an electrically conducting polymer composition described in [1] to [9], the method comprising polymerizing a monomer compound on an oxide dielectric film by an oxidizing agent, which comprises a step of dipping a valve acting metal anode foil having formed thereon an oxide dielectric film layer in a solution containing the monomer compound and a sulfoquinone anion and then dipping the metal anode foil in a solution containing the oxidizing agent.

[16] A method for producing a solid electrolytic capacitor comprising an oxide dielectric film having provided thereon an electrically conducting polymer composition described in [1] to [9], the method comprising polymerizing a monomer compound on an oxide dielectric film by an oxidizing agent, which comprises a step of repeating multiple times a process of dipping a valve acting metal anode foil having formed thereon an oxide dielectric film layer in a solution containing the oxidizing agent and a

sulfoquinone anion and then dipping the metal anode foil in a solution containing the monomer compound.

[0014]

[17] A method for producing a solid electrolytic capacitor comprising an oxide dielectric film having provided thereon an electrically conducting polymer composition described in [1] to [9], the method comprising polymerizing a monomer compound on an oxide dielectric film by an oxidizing agent, which comprises a step of repeating multiple times a process of dipping a valve acting metal anode foil having formed thereon an oxide dielectric film layer in a solution containing the monomer compound and a sulfoquinone anion and then dipping the metal anode foil in a solution containing the oxidizing agent.

[18] A method for producing a solid electrolytic capacitor comprising an oxide dielectric film having provided thereon an electrically conducting polymer composition described in [1] to [9], the method comprising polymerizing a monomer compound on an oxide dielectric film by an oxidizing agent, which comprises a step of repeating multiple times a process of dipping a valve acting metal anode foil having formed thereon an oxide dielectric film layer in a solution containing the oxidizing agent and then dipping the metal anode foil in a solution containing the monomer compound and a sulfoquinone anion.

[19] A method for producing a solid electrolytic capacitor comprising an oxide dielectric film having provided thereon an electrically conducting polymer composition described in [1] to [9], the method comprising polymerizing a monomer compound on an oxide dielectric film by an oxidizing agent, which comprises a step of repeating multiple times a process of dipping a valve acting metal anode foil having formed thereon an oxide dielectric film layer in a solution containing the monomer compound and then dipping the metal anode foil in a solution containing the oxidizing agent and a sulfoquinone anion.

[20] A method for producing a solid electrolytic capacitor comprising an oxide dielectric film having provided thereon an electrically conducting polymer composition described in [1] to [9], the method comprising polymerizing a monomer compound on an oxide dielectric film by an oxidizing agent, wherein a process of dipping a valve acting metal anode foil having formed thereon an oxide dielectric film layer in a solution containing the oxidizing agent and a sulfoquinone anion and then dipping the metal anode foil in a solution containing the monomer compound is repeated multiple times and thereafter the metal anode foil is washed and dried.

[0015]

[21] A method for producing a solid electrolytic

capacitor comprising an oxide dielectric film having provided thereon an electrically conducting polymer composition described in [1] to [9], the method comprising polymerizing a monomer compound on an oxide dielectric film by an oxidizing agent, wherein a process of dipping a valve acting metal anode foil having formed thereon an oxide dielectric film layer in a solution containing the monomer compound and a sulfoquinone anion and then dipping the metal anode foil in a solution containing the oxidizing agent is repeated multiple times and thereafter the metal anode foil is washed and dried.

[22] A method for producing a solid electrolytic capacitor comprising an oxide dielectric film having provided thereon an electrically conducting polymer composition described in [1] to [9], the method comprising polymerizing a monomer compound on an oxide dielectric film by an oxidizing agent, wherein a process of dipping a valve acting metal anode foil having formed thereon an oxide dielectric film layer in a solution containing the oxidizing agent and then dipping the metal anode foil in a solution containing the monomer compound and a sulfoquinone anion is repeated multiple times and thereafter the metal anode foil is washed and dried.

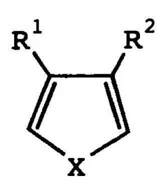
[23] A method for producing a solid electrolytic capacitor comprising an oxide dielectric film having

provided thereon an electrically conducting polymer composition described in [1] to [9], the method comprising polymerizing a monomer compound on an oxide dielectric film by an oxidizing agent, wherein a process of dipping a valve acting metal anode foil having formed thereon an oxide dielectric film layer in a solution containing the monomer compound and then dipping the metal anode foil in a solution containing the oxidizing agent and a sulfoquinone anion is repeated multiple times and thereafter the metal anode foil is washed and dried.

[24] The method for producing a solid electrolytic capacitor as described in [8] or [9], wherein the oxidizing agent is a persulfate.

[25] The method for producing a solid electrolytic capacitor as described in [10] to [23], wherein the oxidizing agent is a persulfate and the monomer compound is a compound represented by the following formula (III):

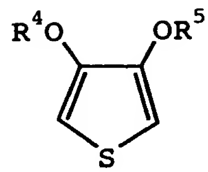
[Chem. 11]



(III)

(wherein R^1, R^2 and X are the same as defined in formula (I)) or a compound represented by the following formula (IV):

[Chem. 12]



(IV)

(wherein R^4 and R^5 are the same as defined in formula (II)).

[0016]

The present invention is described in detail below.

In the present invention, as described in the foregoing, by incorporating into the electrically conducting polymer composition a sulfoquinone anion having one or more sulfoanion groups and a quinone structure in the molecule (hereinafter simply referred to as a "sulfoquinone") as a main anion having a dopant ability and further containing an anion other than a sulfoquinone as an auxiliary dopant, a preferred electrically conducting composition layer (charge-transfer complex) having heat resistance can be formed. As a result, a solid electrolytic capacitor having excellent low impedance property and a production method thereof can be provided.

[0017]

The π electron-conjugated polymer in an electrically conducting polymer composition suitable for the capacitor of the present invention is a polymer having a π electron-conjugated structure in the polymer main chain structure.

Specific examples thereof include polyaniline, poly-p-phenylene, poly-p-phenylenevinylene, polythienylenevinylene, polyheterocyclic polymer and substituted derivatives thereof. Of these specific examples, preferred is a π electron-conjugated polymer comprising a structural unit represented by formula (I), and more preferred is a π electron-conjugated polymer comprising a structural unit represented by formula (II).

[0018]

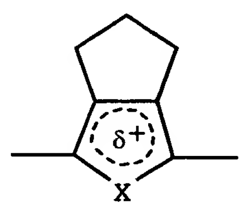
In formulae (I) and (III), useful examples of the linear or branched, saturated or unsaturated hydrocarbon (alkyl) group having from 1 to 6 carbon atoms represented by the substituent R^1, R^2 or R^3 include methyl, ethyl, vinyl, propyl, allyl, isopropyl, butyl and 1-butenyl. Useful examples of the linear or branched, saturated or unsaturated alkoxy group having from 1 to 6 carbon atoms include methoxy, ethoxy, propoxy, isopropoxy and butoxy. Useful examples of the substituent other than the above-described alkyl group or alkoxy group include a nitro group, a cyano group, a phenyl group and a substituted phenyl group (e.g., phenyl group substituted by a halogen group such as Cl, Br, F, etc.). The alkyl group or alkoxy group in R^1 or R^2 may optionally contain in the chain thereof a carbonyl bond, an ether bond, an ester bond, an amide bond or an imino bond, and particularly useful examples thereof

include methoxyethoxy and methoxyethoxyethoxy.

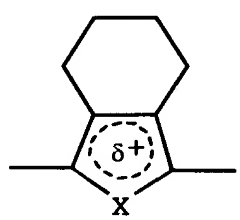
[0019]

The substituents R^1 and R^2 may be combined to each other at any position to form at least one divalent chain for forming at least one 5-, 6- or 7-membered saturated or unsaturated ring structure. Examples of the substitution in formula (I) or (III) include a 3,4-propylene-substituted structure (Chem. 13), a 3,4-butylene-substituted structure (Chem. 14), 3,4-butenylene-substituted structure (Chem. 15), 3,4-butadienylene-substituted structure (Chem. 16) and a naphtho[2,3-c]-condensed structure (Chem. 17).

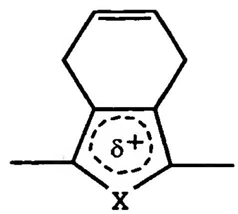
[Chem. 13]



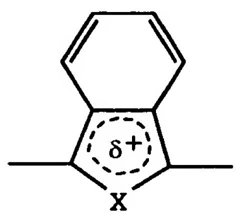
[Chem. 14]



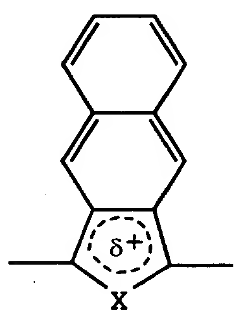
[Chem. 15]



[Chem. 16]



[Chem. 17]



[0020]

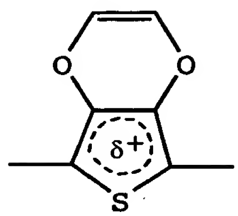
X represents a hetero atom and examples thereof include S, O, Se, Te and NR^3. The above-described 3,4-butadienylene-substituted structure where X is S is called an isothianaphthenylene structure in the case of the monomer compound structure of formula (I) or called isothianaphthene in the case of the monomer compound structure of formula (III). Similarly, the naptho[2,3-c]-

condensed structure is called a naphtho[2,3-c]thienylene structure in the case of formula (I) or called naphtho[2,3-c]thiophene in the case of the monomer compound structure of formula (III). In the formulae, δ represents a number of charges per the repeating structure unit, of from 0 to 1.

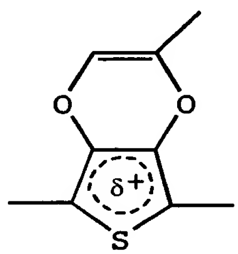
[0021]

Useful examples of the substituents R^4 and R^5 in formulae (II) and (IV) include methyl, ethyl, propyl, isopropyl, vinyl and allyl. Furthermore, R^4 and R^5 may be substituents of which alkyl groups having from 1 to 6 carbon toms are bonded to each other at any position to form at least one or more 5-, 6- or 7-membered heterocyclic ring structure containing the two oxygen elements in formula (II) or (IV). Preferred examples thereof include 1,2-ethylene, 1,2-propylene and 1,2-dimethylethylene. Furthermore, the alkyl groups each having from 1 to 6 carbon atoms of R^4 and R^5 may be combined to each other at any position to form an unsaturated hydrocarbon ring structure such as substituted vinylene group and substituted o-phenylene group, and examples thereof include 1,2-vinylene (Chem. 18), 1,2-propenylene (Chem. 19), 2,3-butylen-2-ene (Chem. 20), 1,2-cyclohexylene (Chem. 21), methyl-o-phenylene (Chem. 22), 1,2-dimethyl-o-phenylene (Chem. 23) and ethyl-o-phenylene (Chem. 24).

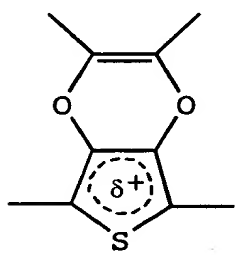
[Chem. 18]



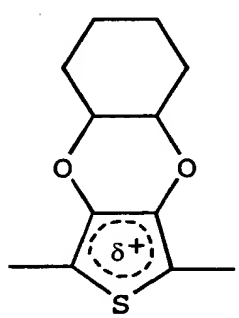
[Chem. 19]



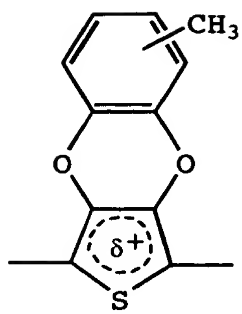
[Chem. 20]



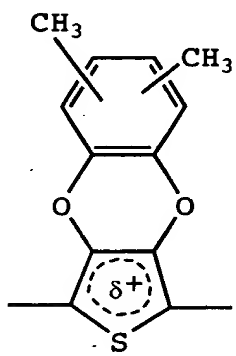
[Chem. 21]



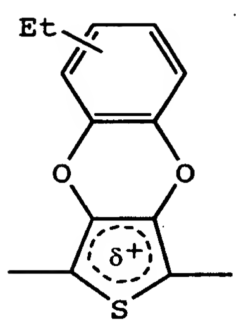
[Chem. 22]



[Chem. 23]



[Chem. 24]



[0022]

Among the monomer compounds represented by formula (III) for use in the solid capacitor and the production process thereof of the present invention, for example

thiophene ($R^1=R^2=H$, X=S) and pyrrole ($R^1=R^2=H$, X=NH), or among thiophenes represented by formula (IV), a monomer compound of 3,4-dioxyethylene-thiophene are known. Also, many of oxidizing agents which can polymerize such a monomer compound are known. However, a capacitor comprising a solid electrolyte formed of an electrically conducting composition containing a sulfoquinone anion as a dopant and using another anion in combination as an auxiliary dopant has heretofore been unknown.

[0023]

To speak more specifically, the capacitor disclosed in JP-A-10-32145 *supra* uses an electrically conducting composition which is a poly(3,4-dioxyethylene-thiophene) having doped therein a specific organic sulfonic acid such as benzoquinonesulfonic acid or alicyclic sulfonic acid, thus, the dopant is only the organic sulfonate anion having a specific chemical structure. This patent publication discloses a technique of providing an organic sulfonate anion from an iron(III) compound used in the oxidizing agent or an anion constituting a cupric compound but addition of an auxiliary dopant is not disclosed therein.

[0024]

The solid electrolytic capacitor of the present invention comprises a solid electrolyte constituted by anions such that the above-described sulfoquinone anion is

contained in an amount of from 0.1 to 50 wt% and another anion in addition to the above-described anion is contained in an amount of from 0.1 to 10 wt%, based on the total weight of the π-conjugated polymer composition, and is particularly characterized by having excellent low impedance property with other problems described above to be solved. Such a capacitor has been heretofore not known. Furthermore, although JP-B-6-101418 *supra* discloses an example of the solid electrolytic capacitor containing as a dopant an anthraquinonesulfonate anion which is one of the sulfoquinone anion, this capacitor has a constitution such that an electrically conducting polymer composition is provided on a valve metal having provided thereon a dielectric film on which manganese dioxide is attached. Thus, the constitution differs from that of the present invention. Moreover, this constitution is disadvantageous in that, as described above, the oxide film layer may be ruptured at the time of formation (thermal decomposition) of the manganese dioxide.

[0025]

The capacitor of the present invention comprises a solid electrolyte capable of providing a capacitor excellent particularly in the low impedance property, wherein the sulfoquinone content is preferably from 1 to 30 wt% based on the total weight of the π-conjugated polymer

composition. On the other hand, in the solid electrolyte of the present invention, the content of another anion in addition to a sulfoquinone anion is preferably from 0.1 to 5 wt% based on the total weight of the polymer composition. In the production method of the present invention, an oxidizing agent is used at the polymerization of a monomer compound, the another anion is contained as a reductant anion of the oxidizing agent, however, it may be added by a different method and the method is not limited.

[0026]

Usually, the method for producing (forming) the above-described solid electrolyte plays an important role in the production of a capacitor for attaining high capacity and high frequency property and improving tan δ, leakage current, heat resistance (reflow property) and durability. To these effects, it is important to densely fill and form an electrically conducting polymer composition layer on a fine dielectric layer to thereby increase or improve the homogeneity of the electric conducting path. In particular, the constitution of the electrically conducting polymer composition has a great effect on the capacity properties.

[0027]

The production method of the present invention is characterized by allowing a sulfoquinone anion and another anion to be present together as dopants for the polymer of

the above-described monomer compound. More specifically, the production method of the present invention comprises a step of producing a polymer composition as the solid electrolyte on the dielectric surface and the polymer composition is produced by causing oxidative polymerization of a monomer compound represented by formula (III) or (IV) on the finely porous dielectric layer in the presence of a compound capable of providing a sulfoquinone anion by the action of the oxidizing agent. By repeating this production process once or more, preferably from 3 to 20 times per one anode substrate, a dense solid electrolyte layer can be easily formed.

[0028]

For example, in one preferred embodiment of the production process, the polymerization step may include a step of dipping a valve-acting metal anode foil having formed thereon an oxide dielectric film layer in a solution containing an oxidizing agent (Solution 1) and a step of dipping the anode foil in a solution containing a monomer compound and a sulfoquinone anion (Solution 2), or may include a step of dipping the anode foil in Solution 2 and then dipping it in Solution 1 or a step of dipping the anode foil in Solution 1 and then dipping it in Solution 2.

In another embodiment, the production step may include a step of dipping the anode foil in a solution containing

an oxidizing agent and a sulfoquinone anion (Solution 3) and a step of dipping the anode foil in a solution containing a monomer compound (Solution 4) or may include a step of dipping the anode foil in Solution 4 and then dipping it in Solution 3 or a step of dipping the anode foil in Solution 3 and then dipping it in Solution 4. Solution 1 to 4 each may be used in the form of a suspension.

[0029]

Furthermore, the dipping process may be replaced to the coating operation. Solutions 1 to 4 may be the same, if desired, or may be different solvent systems. According to the kind of the solvent, a drying step may be additionally provided between the process of Solution 1 and Solution 2 or between the process of Solution 3 and Solution 4. After producing the solid electrolyte, a step of washing the device with an organic solvent or with water may be provided. In this case, it is simple and preferred to use the solvent used in any of Solutions 1 to 4 as the organic solvent for use in the washing, however, any solvent may be used as far as it can merely dissolve the monomer compound, the sulfoquinone compound or the compound providing another anion having a dopant ability.

[0030]

The above-described repetition of oxidation

polymerization process facilitates the production of a solid electrolyte having excellent soldering heat resistance (heat stability). In conventionally known capacitors using a solid electrolyte comprising polypyrrole or the like, the capacitor properties greatly fluctuate at a high temperature and a high humidity and the reliability is low, however, the capacitor comprising a solid electrolyte formed with an electrically conducting composition of the present invention has excellent heat stability and exhibits good stability in the doped state, because the polymer composition having the above-described two or more dopants can be thoroughly filled step by step into the dielectric surface and even inside the pore, and thereby a structure where many thin films of the polymer composition are overlaid one on another can be formed. As a result, a capacitor having excellent heat stability such that the dielectric film is prevented from damages by the polymer can be provided.

[0031]

The sulfoquinone anion used in the present invention is a compound anion having a chemical structure such that ketone groups in a quinone structure and a sulfonic acid group as an electron withdrawing group are bound as the substituents within the same molecule. Accordingly, this anion differs from conventionally known molecular anions

(e.g., ClO_4^-, BF_4^-, Cl^-, SO_4^{2-}, etc.) in the dopant ability (e.g., stability of the charge transfer complex, electric conductivity) and the chemical properties, and further exhibits superior effects as compared with the system of using a conventionally known molecular anion (e.g., ClO_4^-, BF_4^-, Cl^-, SO_4^{2-}, etc.) alone. More specifically, when a plurality of capacitor devices are manufactured and compared, particularly excellent effects can be brought out on the capacitor performance.

[0032]

The sulfoquinone used in the present invention is a generic term of compounds having one or more sulfonic acid groups and a quinone structure within the molecule and any may be used as far as it has a chemical structure of allowing effective working as a dopant in the form of the sulfonate anion. Examples of the sulfoquinone basic skeleton include p-benzoquinone, o-benzoquinone, 1,2-naphthoquinone, 1,4-naphthoquinone, 2,6-naphthoquinone, 9,10-anthraquinone (hereinafter simply referred to as an "anthraquinone"), 1,4-anthraquinone, 1,2-anthraquinone, 1,4-chrysenequinone, 5,6-chrysenequinone, 6,12-chrysenequinone, acenaphthoquinone, acenaphthenequinone, camphorquinone, 2,3-bornanedione, 9,10-phenanthrenequinone and 2,7-pyrenequinone

Furthermore, the sulfonic acid group in the above-

described sulfoquinone includes an aromatic sulfonic acid structure resulting from replacing one or more hydrogens of the quinone compound by a sulfonic acid group, or an aliphatic sulfonic acid structure resulting from replacement by sulfoalkylene group through a divalent saturated or unsaturated hydrocarbon group having from 1 to 12 carbon atoms. Also, a chemical structure resulting from replacing one or more hydrogens of the sulfoquinone by a saturated or unsaturated alkyl or alkoxy group having from 1 to 12 carbon atoms, preferably from 1 to 6 carbon atoms, or by a substituent selected from F, Cl and Br may also be used.

[0033]

In particular, the sulfoquinone for use in the present invention is preferably a sulfoquinone having a skeleton of anthraquinone, 1,4-naphthoquinone or 2,6-naphthoquinone. Examples of anthraquinones which can be used include anthraquinone-1-sulfonic acid, anthraquinone-2-sulfonic acid, anthraquinone-1,5-disulfonic acid, anthraquinone-1,4-disulfonic acid, anthraquinone-1,3-disulfonic acid, anthraquinone-1,6-disulfonic acid, anthraquinone-1,7-disulfonic acid, anthraquinone-1,8-disulfonic acid, anthraquinone-2,6-disulfonic acid, anthraquinone-2,3-disulfonic acid, anthraquinone-2,7-disulfonic acid, anthraquinone-1,4,5-trisulfonic acid, anthraquinone-

2,3,6,7-tetrasulfonic acid, and/or an alkali metal salt and/or ammonium salt thereof.

[0034]

Examples of 1,4-naphthoquinones which can be used include 1,4-naphthoquinone-5-sulfonic acid, 1,4-naphthoquinone-6-sulfonic acid, 1,4-naphthoquinone-5,7-disulfonic acid, 1,4-naphthoquinone-5,8-disulfonic acid, and/or an alkali metal and/or ammonium salt thereof.

Examples of 2,6-naphthoquinones which can be used include 2,6-naphthoquinone-1-sulfonic acid, 2,6-naphthoquinone-3-sulfonic acid, 2,6-naphthoquinone-4-sulfonic acid, 2,6-naphthoquinone-3,7-disulfonic acid, 2,6-naphthoquinone-4,8-disulfonic acid, and/or an alkali metal and/or ammonium salt thereof.

The sulfoquinone further may be selected from industrial dyes and examples thereof include Anthraquinone Iris R and Anthraquinone Violet RN-3RN. These industrial dyes each may also be used as a useful sulfoquinone-based dopant in the form of the above-described salt.

[0035]

The sulfoquinone for use in the present invention participates into the polymerization reaction of the monomer compound depending on the compound and acts as one oxidative dehydrogenating agent. A proton adduct of the quinone structure, namely a hydroquinone structure, or

quinhydron resulting from the reduction of the sulfoquinone in the polymerization reaction may be contained as it is as a dopant in the solid electrolyte.

[0036]

The oxidizing agent for use in the present invention may be any oxidizing agent suitable for the oxidation polymerization of pyrrole or thiophenes. Examples of the oxidizing agent which can used include oxidizing agents over a wide range, such as iron(III) chloride, $Fe(ClO_4)_3$, organic acid iron(III), inorganic acid iron(III), alkylpersulfate, ammonium persulfate, hydrogen peroxide and $K_2Cr_2O_7$ described in JP-A-2-15611. Examples of the organic acid iron(III) include an alkylsulfonic acid having from 1 to 20 carbon atoms such as methanesulfonic acid and dodecylbenzenesulfonic acid, and an aliphatic carboxylic acid having from 1 to 20 carbon atoms. However, the oxidizing agent may be restricted in the range of use by the chemical structure of the monomer compound represented by formula (III), the oxidizing agent, reaction conditions and the like. For example, according to Handbook of Conducting Polymers, page 99, Marcel Dekker, Inc. (1987), Fig. 5, the kind of the substituent greatly affects the oxidation potential (one index for showing whether the polymerization readily or difficultly occurs) and in turn, governs the oxidation (polymerization) of thiophenes

(oxidation potential expands over a wide range of from about 1.8 to about 2.7 V). Accordingly, in practice, the combination of the monomer compound and oxidizing agent used and the reaction conditions is important.

[0037]

The anion other than the sulfoquinone anion is a reductant anion after the reaction of the oxidizing agent and specific examples thereof include chloride ion, ClO_4^-, aliphatic organic carboxylate anion having from 1 to 12 carbon atoms, sulfate ion, phosphate anion, aliphatic organophosphate anion having from 1 to 12 carbon atoms and borate anion. Furthermore, an electron acceptor dopant such as NO^+ and NO_2^+ salt (e.g., $NOBF_4$, $NOPF_6$, $NOSbF_6$, $NOAsF_6$, $NOCH_3SO_3$, NO_2BF_4, NO_2PF_6, $NO_2CF_3SO_3$) may also be used.

[0038]

In the production method of a solid electrolytic capacitor of the present invention, the chemical polymerization of a thiophene represented by formula (IV) is particularly preferably performed using a persulfate. The use of iron(III) salt-based oxidizing agent has a problem in that an iron element remains and adversely affects the capacitor properties. Persulfates suitable for the monomer compound represented by formula (IV) are not suitable for the thiophene represented by formula (III) (R^1=R^2=H, X=S) and thus, the use of the oxidizing agent has

a restriction. Examples of the persulfate which can be particularly suitably used for the chemical polymerization of a thiophene represented by formula (IV) include ammonium persulfate and potassium persulfate.

[0039]

Preferred conditions for the producing (polymerization) reaction are described below.

The concentration of the monomer compound represented by formula (III) or (IV) for use in the production method of a capacitor of the present invention and the concentrations of the oxidizing agent and the sulfoquinone used vary depending on the kind of the compound or substituents thereof and the combination with a solvent or the like, however, it is in general from 1×10^{-4} to 10 mol/ℓ, preferably from 1×10^{-3} to 5 mol/ℓ. The reaction temperature is selected according to respective reaction processes and cannot be specifically limited, however, it is generally from -70 to 250°C, preferably from 0 to 150°C and more preferably from 15 to 100°C.

[0040]

Examples of the solution for use in the production method of the present invention or the solvent for use in washing after the polymerization include tetrahydrofuran (THF), dioxane, ethers such as diethyl ether, ketones such as acetone and methyl ethyl ketone, aprotic polar solvents

such as dimethylformamide, acetonitrile, benzonitrile, N-methylpyrrolidone (NMP) and dimethylsulfoxide (DMSO), esters such as ethyl acetate and butyl acetate, nonaromatic chlorine-type solvents such as chloroform and methylene chloride, nitro compounds such as nitromethane, nitroethane and nitrobenzene, alcohols such as methanol, ethanol and propanol, organic acids such as formic acid, acetic acid and propionic acid, acid anhydrides of the organic acid (e.g., acetic anhydride), water, and a mixed solvent thereof. Of these, preferred are water, an alcohol, a ketone and/or a combination thereof.

[0041]

The solid electrolyte thus produced has an electric conductivity of from 0.1 to 200 S/cm, preferably from 1 to 100 S/cm, more preferably from 10 to 100 S/cm.

In the present invention, for one part electrode, a known material such as a foil or bar having a valve action of aluminum, titanium, tantalum, niobium or an alloy using such a material as a substrate, or a sintered body mainly comprising such a material. This metal electrode is used after treating the surface thereof by a known method such as etching or chemical forming so as to increase the specific surface area, and thereby forming a metal oxide film layer on the metal foil.

[0042]

The solid electrolyte is preferably formed by effecting the producing process on the dielectric layer. In particular, a method of chemically depositing an organic electric conductor having excellent heat resistance of the present invention on a dielectric material having a porous or void structure is preferred. Furthermore, in order to attain good electrical contacting, an electric conductor layer is preferably provided on the semiconductor and the electric conductor layer is formed, for example, by solidifying or plating an electrically conducting paste, sputtering a metal or forming an electrically conducting resin film.

The capacitor thus constituted according to the production method of the present invention is jacketed with a resin mold, a resin case or a metal-made jacket case or by resin dipping and then the capacitor can be used as a product capacitor for various uses.

[0043]

[Examples]

The present invention is described in greater detail below by referring to the Examples and Reference Examples.

(Example 1)

A formed aluminum foil was processed to have a prescribed area and then subjected to forming at 13 V in an

aqueous 10 wt% ammonium adipate solution to prepare a dielectric material on the aluminum foil. The surface of this dielectric material was impregnated with an aqueous solution prepared to have an ammonium persulfate (hereinafter simply referred to as "APS") concentration of 20 wt% and a sodium anthraquinone-2-sulfonate concentration of 0.1 wt% (Solution 3), and then the dielectric foil was dipped in 1.2 mol/ℓ of an isopropanol (hereinafter simply referred to as "IPA") solution having dissolved therein 5 g of 3,4-dioxyethylene-thiophene (Solution 4). The resulting substrate was taken out and left standing in an environment at 60°C for 10 minutes, thereby completing the oxidative polymerization, and then the substrate was washed with water. This polymerization reaction and washing process each was repeated 10 times. The polymer composition was compensated with hydrazine in a water/IPA solvent and then carefully extracted and the contents of sulfate ion and anthraquinone-2-sulfonate ion in the polymer composition were determined by an ion chromatography method. As a result, the sulfate ion content was 1.1 wt% and the anthraquinone-2-sulfonate ion content was 34 wt%, based on the dry weight of the polymer composition. The solid electrolyte layer had an electric conductivity of 75 S/cm.

[0044]

Thereafter, an aluminum foil having deposited thereon

the polythiophene composition was treated in an aqueous 10 wt% ammonium adipate solution and then examined on the sparking voltage. The test was performed by increasing the number of devices (the same in the following Examples) so as to attain distinguished comparison of the device properties, namely, in an environment of 50°C under the conditions of a current density of 10 mA/cm^2 in n=5 times. The results obtained are shown in Table 1. Subsequently, the aluminum core part was welded with a plus side lead terminal for collecting the current from the anode and on the other hand, connected to the minus side lead terminal through carbon paste and silver paste for collecting the current from the cathode. These elements were finally sealed by an epoxy resin to manufacture a capacitor device. The capacitor device manufactured was aged at 125°C for 2 hours and then subjected to the initial evaluation. The results obtained are shown together in Table 2. In the Table, C in the column of initial characteristics indicates a capacity and DF indicates a tangent (tan δ) of the loss angle. These were each measured at 120 Hz. The impedance is shown by a value at a resonance frequency. LC (leakage current) was measured one minute after applying a rated voltage. The measured values each is an average of 30 samples. With respect to LC, those having an LC of 1 μA or more are judged as a defective and those having an LC of 10

μA or more are judged as a shorted product. The average LC is calculated exclusive of the defective units.

[0045]

(Example 2)

A formed aluminum foil was processed to have a prescribed area and then subjected to forming at 13 V in an aqueous 10 wt% ammonium adipate solution to prepare a dielectric material. The surface of this dielectric material was impregnated with an aqueous solution prepared to have an APS concentration of 20 wt% (Solution 1) and then dipped in an IPA/water mixed solution prepared by adding ammonium anthraquinone-2,6-disulfonate to 1.2 mol/ℓ of an IPA solution having dissolved therein 5 g of 3,4-dioxyethylene-thiohene to have an ammonium anthraquinone-2,6-disulfonate concentration of 0.1 wt% (Solution 2). The resulting substrate was taken out and left standing in an environment at 60°C for 10 minutes, thereby completing the oxidative polymerization, and then the substrate was washed with water. This polymerization reaction and washing process each was repeated 10 times. The capacitor device obtained was evaluated. The results obtained are shown in Tables 1 and 2. The contents of sulfate ion and anthraquinone-2,6-disulfonate ion in the polymer composition were determined by the method described in Example 1. As a result, the sulfate ion content was 1.3 wt%

and the anthraquinone-2,6-disulfonate ion content was 31 wt%. The solid electrolyte layer had an electric conductivity of 80 S/cm.

[0046]

(Example 3)

A formed aluminum foil was processed to have a prescribed area and then subjected to forming at 13 V in an aqueous 10 wt% ammonium adipate solution to prepare a dielectric material. This dielectric material was dipped in 1.2 mol/ℓ of an IPA solution having dissolved therein 5 g of 3,4-dioxyethylene-thiophene (Solution 4) and then dipped in an aqueous solution prepared to have an APS concentration of 20 wt% and a sodium 1,4-naphthoquinone-2-sulfonate concentration of 0.1 wt% (Solution 3). The resulting substrate was taken out and left standing in an environment at 60°C for 10 minutes, thereby completing the oxidative polymerization, and then the substrate was washed with water. This polymerization reaction and washing process each was repeated 10 times. The capacitor device obtained was evaluated and the results obtained are shown in Tables 1 and 2. The contents of sulfate ion and 1,4-naphthoquinone-2-sulfonate ion in the polymer composition were determined by the method described in Example 1. As a result, the sulfate ion content was 1.0 wt% and the 1,4-naphthoquinone-2-sulfonate ion content was 28 wt%. The

solid electrolyte layer had an electric conductivity of 68 S/cm.

[0047]

(Example 4)

A formed aluminum foil was processed to have a prescribed area and then subjected to forming at 13 V in an aqueous 10 wt% ammonium adipate solution to prepare a dielectric material. The surface of this dielectric material was impregnated with an aqueous solution prepared to have a potassium persulfate concentration of 10 wt% and a sodium anthraquinone-2-sulfonate concentration of 0.1 wt% (Solution 3) and then dipped in 1.2 mol/ℓ of an IPA solution having dissolved therein 5 g of 3,4-dioxyethylene-thiophene (Solution 4). The resulting substrate was taken out and left standing in an environment at 60°C for 10 minutes, thereby completing the oxidative polymerization. This polymerization reaction comprising the above process was repeated 10 times and then the substrate was washed with water and dried. The capacitor device obtained was evaluated and the results obtained are shown in Tables 1 and 2. The contents of sulfate ion and anthraquinone-sulfonate ion in the polymer composition were determined by the method described in Example 1. As a result, the sulfate ion content was 2.0 wt% and the anthraquinone-2-sulfonate ion content was 30.0 wt%. The solid electrolyte layer had

an electric conductivity of 69 S/cm.

[0048]

(Example 5)

A formed aluminum foil was processed to have a prescribed area and then subjected to forming at 13 V in an aqueous 10 wt% ammonium adipate solution to prepare a dielectric material. The surface of this dielectric material was impregnated with an aqueous solution prepared to have an APS concentration of 35 wt% (Solution 1) and then dipped in an IPA/water mixed solution having an ammonium anthraquinone-2,6-disulfonate concentration of 0.04 wt% (Solution 2) prepared by adding ammonium anthraquinone-2,6-disulfonate to an IPA solution of 1.2 mol/ℓ having dissolved therein 5 g of 3,4-dioxyethylen e-thiophene. The resulting substrate was taken out and left standing in an environment at 60°C for 10 minutes, thereby completing the oxidative polymerization. This polymerization reaction comprising the above process was repeated 10 times and then the substrate was washed with water and dried. The capacitor device obtained was evaluated and the results obtained are shown in Tables 1 and 2. The contents of sulfate ion and anthraquinone-2,6-disulfonate ion in the polymer composition were determined by the method described in Example 1. As a result, the sulfate ion content was 4.5 wt% and the anthraquinone-2,6-

disulfonate ion content was 9.2 wt%. The solid electrolyte layer had an electric conductivity of 50 S/cm.

[0049]

(Example 6)

A formed aluminum foil was processed to have a prescribed area and then subjected to forming at 13 V in an aqueous 10 wt% ammonium adipate solution to prepare a dielectric material. This dielectric material was dipped in a degassed IPA solution of 5,6-dimethoxy-isothianaphthene synthesized and produced by sublimation according to the method described in JP-A-2-242816 wherein the concentration of the compound was 1.2 mol/ℓ (Solution 4) and then dipped in 20 wt% of aqueous APS solution of sodium 3-methyl-2-anthraluinolylmethanesulfonate synthesized according to the method described in <u>Tetrahedron</u>, Vol. 35, No. 19, page 2263 (1979) wherein the concentration of the sodium 3-methyl-2-anthraquinolylmethanesulfonate was adjusted to be 0.1 wt% in the aqueous solution (Solution 3). The resulting substrate was taken out and left standing in an environment at 60°C for 10 minutes, thereby completing the oxidative polymerization. This polymerization reaction comprising the above process was repeated 10 times and then the substrate was washed with water and dried. The capacitor device obtained was evaluated and the results obtained are shown in Tables 1 and 2. The contents of sulfate ion and 3-

methyl-2-anthraquinolylmethanesulfonate ion in the polymer composition were determined by the method described in Example 1. As a result, the sulfate ion content was 0.5 wt% and the 3-methyl-2-anthraquinolylmethanesulfonate ion content was 4.8 wt%. The solid electrolyte layer had an electric conductivity of 40 S/cm.

[0050]

(Example 7)

A capacitor device was prepared and evaluated in the same manner as in Example 1 except for using a solution of pyrrole-N-methyl prepared to have the same concentration in place of 3,4-dioxyethylene-thiophene used in Example 1. The results obtained are shown in Tables 1 and 2. The contents of sulfate ion and anthraquinone-2-sulfonate ion in the polymer composition were determined by the method described in Example 1. As a result, the sulfate ion content was 7.5 wt% and the anthraquinone-2-sulfonate ion content was 20.3 wt%. The solid electrolyte had an electric conductivity of 8 S/cm.

[0051]

(Example 8)

A formed aluminum foil was processed to have a prescribed area and then subjected to forming at 13 V in an aqueous 10 wt% ammonium adipate solution to prepare a dielectric material. This dielectric material was dipped in

a 30% DMF-IPA solution prepared to have a sodium anthraquinone-2-sulfonate concentration of 0.1 wt% and a 3,4-dioxyethylene-thiophene concentration of 1.2 mol/ℓ (Solution 2) and then dipped in a 20 wt% aqueous APS solution (Solution 1). The resulting substrate was taken out and left standing in an environment at 60°C for 10 minutes, thereby completing the oxidative polymerization. These dipping processes each was repeated 10 times and then the substrate was washed with water and dried. The capacitor device obtained was evaluated and the results obtained are shown in Tables 1 and 2. The sulfate ion content was 1.2 wt% and the anthraquinone-2-sulfonate ion content was 37 wt%, based on the dry weight of the polymer composition. The solid electrolyte layer had an electric conductivity of 80 S/cm.

[0052]

(Example 9)

A process for manufacturing a capacitor device was performed under the same conditions as in Example 1 except for using thiophene in place of 3,4-dioxyethylene-thiophene used in Example 1. However, black blue polythiophene was not produced at all and thus, polymerization of thiophene was not caused by the action of APS. In other words, occurrence of the oxidation polymerization of a thiophene by APS was peculiar to 3,4-dioxy group-substituted

thiophenes.

[0053]

(Comparative Example 1)

A formed dielectric material was prepared in the same manner as in Example 1 and the dielectric material obtained was dipped in a 12% IPA solution of ferric anthraquinone-2-sulfonate and then dipped in 1.2 mol/ℓ of an IPA solution having dissolved therein 5 g of 3,4-dioxyethylene-thiophene. The resulting substrate was left standing in an environment at 60°C for 10 minutes, thereby completing the oxidative polymerization, and then the substrate was washed with water. This polymerization reaction and washing process each was repeated 10 times. The polymer composition was compensated with hydrazine in a water/IPA solvent and then carefully extracted and the content of anthraquinone-2-sulfonate ion in the polymer composition was determined by an ion chromatography method. As a result, the anthraquinone-2-sulfonate ion content was 25 wt% based on the dry weight of the polymer composition. The solid electrolyte layer had an electric conductivity of 30 S/cm. Thereafter, a capacitor device was manufactured and examined on the sparking voltage and other capacitor properties in the same manner as in Example 1. The results obtained are shown in Tables 1 and 2.

[0054]

(Comparative Example 2)

A capacitor device was prepared and evaluated in the same manner as in Example 1 except for changing the concentration of APS used in Example 1 from 20 wt% to 12 wt%. The results obtained are shown in Tables 1 and 2. The contents of sulfate ion and anthraquinone-2-sulfonate ion in the polymer composition were determined by the method described in Example 1. As a result, the sulfate ion content was 0.09 wt% and the anthraquinone-2,6-disulfonate ion content was 32 wt%. The solid electrolyte had an electric conductivity of 40 S/cm.

[0055]

(Comparative Example 3)

A capacitor device was prepared and evaluated in the same manner as in Example 1 except for using a solution prepared to have a ferric sulfate concentration of 10 wt% and a sodium anthraquinone-2-sulfonate concentration of 0.1 wt% in place of APS used in Example 1. The results obtained are shown in Tables 1 and 2. The contents of sulfate ion and anthraquinone-2-sulfonate ion in the polymer composition were determined by the method described in Example 1. As a result, the sulfate ion content was 20.0 wt% and the anthraquinonesulfonate ion content was 37.8 wt%. In the polymer composition, 8 wt% of iron ion

(ferric and ferrous) was present and the sulfate ion content exceeded 10 wt%, as a result, the capacitor exhibited poor properties.

[0056]

(Comparative Example 4)

A capacitor device was prepared and evaluated in the same manner as in Example 1 except for using thiophene in place of 3,4-dioxyethylene-thiohene used in Example 1 and preparing a solution to have a concentration of ferric chloride used in place of APS, of 10 wt% and a sodium anthraquinone-2-sulfonate concentration of 0.1 wt%. The results obtained are shown in Tables 1 and 2. The anthraquinone-2-sulfonate ion content in the polymer composition was determined by the method described in Example 1 and found to be 4.2 wt%. Since sulfate ion was not used in combination, the capacitor exhibited poor properties.

[0057]

In the sparking voltage test of Examples 1 to 8, the voltage was scarcely reduced and at the completion of the reaction, the sparking voltage was 19 V or less in each Example. In Comparative Example 3 using ferric sulfate, the sparking voltage was largely reduced due to remaining of iron ion (ferric and ferrous ions) in a concentration as high as 8 wt% and the sparking voltage could not withstand

until the prescribed reaction (operation) was completed. As a result, the solid electrolyte was insufficiently filled and this was disadvantageous.

[0058]

[Table 1]

Sparking Voltage (unit: V, n=5)

	Number of Reaction Times							
	1	2	3	4	5	6	8	10
Example 1	19	19	19	19	19	19	19	19
Example 2	19	19	19	19	19	19	19	19
Example 3	19	19	19	19	19	19	19	19
Example 4	19	19	19	18	17	15	13	10
Example 5	19	19	19	19	19	19	19	19
Example 6	19	19	19	19	19	19	19	19
Example 7	19	19	19	19	19	19	19	19
Example 8	19	19	19	19	19	19	19	19
Comparative Example 1	19	16	13	5	2			
Comparative Example 2	19	19	19	19	19	19	19	19
Comparative Example 3	19	17	13	3				
Comparative Example 4	18	15	11	3				

[0059]

[Table 2]

	Initial Characteristics					
	C µF	DF %	Z mΩ	LC µA	Number of Defective/Number of Sample units/units	Short Circuit
Example 1	8.0	0.7	60	0.02	0/30	0
Example 2	8.2	0.7	60	0.02	0/30	0
Example 3	7.5	0.8	60	0.03	0/30	0
Example 4	7.0	0.8	60	0.04	1/30	0
Example 5	6.9	0.9	60	0.05	1/30	0
Example 6	6.8	0.8	60	0.05	1/30	0
Example 7	4.1	1.2	60	0.09	1/30	0
Example 8	8.1	0.7	60	0.02	1/30	0
Comparative Example 1	7.1	1.2	60	0.15	10/30	8
Comparative Example 2	7.0	0.7	60	0.09	1/30	0
Comparative Example 3	6.1	3.2	83	0.40	15/30	10
Comparative Example 4	5.9	3.3	90	0.43	27/30	18

[0060]

[Effect of the Invention]

As described in the foregoing, the solid electrolytic capacitor of the present invention comprises a solid electrolyte containing a sulfoquinone having one or more

sulfoanion groups and a quinone structure within the molecule and containing in combination another anion having a dopant ability as a dopant in addition to the above-described sulfoquinone anion, whereby a compact, low-impedance and high-performance solid electrolytic capacitor and a production method thereof can be provided.

Furthermore, the solid electrolytic capacitor of the present invention comprises a solid electrolyte using a specific polyheterocyclic compound, particularly an electrically conducting polythiophene as a π electron-conjugated polymer and thereby, an effect is provided such that the voltage withstanding property (sparking voltage test), high frequency property, tan δ, impedance property, leakage current, heat resistance (reflow property) and the like are greatly improved. In particular, the above-described electrically conducting polymer composition has a sulfoquinone content of from 0.1 to 50 wt% and a sulfate content of from 0.1 to 10 wt% and as a result thereof, a solid electrolytic capacitor having high-performance capacitor properties can be provided.

[NAME OF DOCUMENT] Abstract

[SUMMARY]

[PROBLEM TO BE SOLVED]

To provide a solid electrolytic capacitor having excellent properties with respect to the voltage withstanding property, high frequency property, tan δ, leakage current, heat resistance (reflow property) and the like.

[MEANS TO SOLVE THE PROBLEM]

The above-described problem has been solved by a solid electrolytic capacitor obtained by forming an electrically conducting polymer composition on the surface of an oxide film layer formed on a valve acting metal, wherein the solid electrolyte contains from 0.1 to 50 wt% of a sulfoquinone as a main dopant and from 0.1 to 10 wt% of another anion having a dopant ability.

[SELECTED DRAWING] None.